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Temperature-controlled hydrothermal synthesis of a 2D ferromagnetic coordination bilayered polymer and a novel 3D network with inorganic Co$_3$(OH)$_2$ ferrimagnetic chains†

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A 2D bilayered ferromagnetic coordination polymer, generated by lower-temperature hydrothermal reactions of cobalt(II) salt with the 3,4-pyridinedicarboxylate dianion, was controlled to transform into a 3D magnetic coordination network with Co$_3$(OH)$_2$ ferrimagnetic chains at a higher temperature.

The rapidly expanding field of crystal engineering of two- (2D) and three-dimensional (3D) coordinated polymers is of great current interest for both the structural and topological novelty as well as for their potential application as functional materials.[1] The main strategy popularly used in this area is a building-block approach.[2] The versatility of organic functional groups (such as 4,4′-bipyridine, polycarboxylic acids) and the diversity of metal-hydroxide units have led to a wide array of functional organic–inorganic hybrid materials.[2–6] Pyridine-*n,m*-dicarboxylic acid (*n,m*-pyda, *n,m* = 2 ~ 4) seems to be an excellent building block with charge and multi-connecting ability, that has not, to our knowledge, been well documented as the connector in the design of functional coordination polymers.[7–9] Of particular interest to us is the exploration of function-structural correlations in the transition metal compounds of *n,m*-pyda (*n,m* = 2 ~ 4) with theoretically important topologies. In this communication we report two interesting coordination polymers, one is a 2D ferromagnetic coordination bilayered polymer, [Co(3,4-pyda)(H$_2$O)$_2$]$_n$·nH$_2$O **1**, and the another is 3D magnetic coordination polymer with inorganic Co$_3$(OH)$_2$ ferrimagnetic chains, [Co$_3$(OH)$_2$(3,4-pyda)$_2$(H$_2$O)$_2$]$_n$ **2**.

Reactions of CoCl$_2$·6H$_2$O (1.0 mmol) with 3,4-pyda (1.0 mmol) and NaOH (2.0 mmol) in water (10 ml) at 150 °C for 24 hours yield very fine purple plate crystals of **1** in 70% yield. It is interesting to note that when the above-mentioned reaction was carried out at 150 °C for 24 hours and then at 180 °C for another 24 hours, a deep purple crystalline product of **2** was isolated (yield 60%). Parts of the aqua molecules were obviously deprotonated into hydroxide groups at higher temperature, which is a key to the formation of **2**. Performing the similar above-mentioned reaction at lower temperatures between 155 and 175 °C only led to the formation of single phase of **1**. Phase purity of the bulk material was confirmed by comparison of its powder diffraction pattern with that calculated from the single crystal study.

X-Ray structural analysis‡ shows that **1** crystallizes in triclinic with an asymmetric unit consisting of one formula unit and therefore there is only one metal environment. The cobalt(II) ion is coordinated in an octahedral geometry with a NO$_5$ donor set (Fig. 1a) coming from four different 3,4-pyda ligands and two aqua molecules. Each ligand is coordinated to four metal atoms to form a bilayered coordination polymer with an interesting approximately extended triangular lattice in the *ab*-plane. One carboxylate group of each 3,4-pyda coordinates the Co(II) through a single O1 atom in

the *ab*-plane, another carboxylate group acts as a non-coplanar *syn–anti O,O′*-bridge (Fig. 1c), resulting in a coordination bilayered structure with an approximate triangular lattice (Figs. 2a, S1 and S2†). Extensive hydrogen bonds are formed among lattice water molecules, coordinated water molecules and the carboxylate oxygens of adjacent bilayers (O(w)···O (carboxylato) 2.706(3)–2.868(3) Å), linking the adjacent bilayers into a 3D hydrogen bond network (Fig. S3). It is interesting that the Co(OCO)Co dimers that are present within bilayers allow for an efficient magnetic interaction between the Co centres propagated through the carboxylate bridges. The Co···Co distance within the dimer is 4.773 Å while the shortest Co···Co distances within the monolayer is 7.111–9.269 Å (Fig. 2b) through the pyda bridges.

2 also crystallizes in triclinic with an asymmetric unit consisting of half a formula unit and therefore there are two crystallographically independent Co(II) atoms, a symmetry related pair of
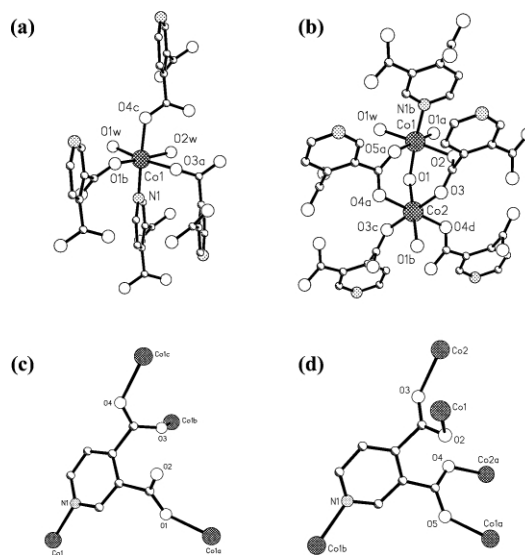

Fig. 1 The metal–ligand building blocks showing all the metals coordinated to one ligand and all the ligands coordinated to one metal. For **1**: (a) and (c); for **2**: (b) and (d).
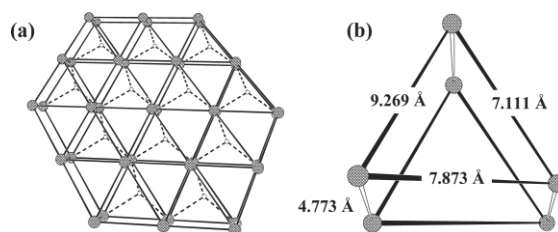

Fig. 2 (a) Perspective view showing the Co–Co connections in the bilayered structure of **1**. Small open balls represent centres of mass of the pyda ligands and only the centres of mass of single layer are shown for clarity. (b) The Co–Co distances within the triangular units.

Co1 and Co1a separated by 2.988 Å that alternates with Co(2), located on a centre of symmetry (Fig. 3a). The Co1 atom is coordinated in an octahedral $CoNO_5$ geometry (Fig. 1b) to two carboxylate O atoms and one pyridyl N atom coming from three different 3,4-pyda ligands, two OH^- groups and one aqua molecules. The Co2 atom, situated at a special position, coordinates in an octahedral CoO_6 geometry with four carboxylate O atoms and two OH^- groups. Each pyda ligand is coordinated to five metal atoms (Fig. 1d), and both carboxylate groups of each 3,4-pyda coordinate in *syn–syn O,O'*-bridging mode. Of marked interest is that the whole structure is a 3D coordination network (Fig. 3b) consisting of 1D $Co_3(OH)_2$ chains and 3,4-pyda bridges. The repeating trimeric structural unit in the cobalt hydroxide chain consists of two edge-sharing symmetry-related cobalt octahedra (Co1–Co1a) linked *via* μ_3-OH to a vertex of Co2 octahedron (Fig. 3a). The Co1–Co2 and Co1a–Co2 distances are 3.552 and 3.857 Å, thus forming an irregular triangle. The Co1–OH–Co1a angle is 91.8°, while Co1–OH–Co2 angles are 114.8 and 134.2°. A few structurally characterized compounds containing Co(II) hydroxide units and polyfunctional ligands have been reported so far. However, the bridging spacers were focused on bi-, tri- and tetracarboxylate ligands.[5,7,8] The present structure represents a unique example of 3D networks with metal hydroxide chains spaced by 3,4-pyridyldicarboxylate.

The magnetic behaviours of **1** and **2** are displayed in Fig. 4. For **1**, the value of the magnetic moment (μ_{eff}) at room temperature is 6.01 μ_B per Co formula unit. Upon lowering the temperature, μ_{eff} gradually increases from 6.01 μ_B at 300 K to 7.05 μ_B at 10.0 K, showing a significant ferromagnetic interaction. Upon a further decrease of temperature, however, the μ_{eff} decreases quickly due to the presence of zero-field splitting. The magnetic susceptibility obey the Curie–Weiss law above 50 K with a Weiss constant, θ = 8.30 K, and a Curie constant, C = 4.39 $cm^3\ mol^{-1}$ K, indicates a significant ferromagnetic coupling between the dimeric Co(II) S = 3/2 spins through the *syn–anti* carboxylato bridges.[10] For **2**, through cooling from room temperature to 50 K, a first decrease of the values of μ_{eff} is observed, followed by an important and sharp increase of μ_{eff} down to 16 K (Fig. S5). This shows an existence of relatively weak antiferromagnetic interaction in this magnetic system, and the small decrease indicates competition between two spin-up centres and one spin-down centre in the $Co_3(OH)_2$ magnetic chains. Considering the 1D cobalt-hydroxide chain, the
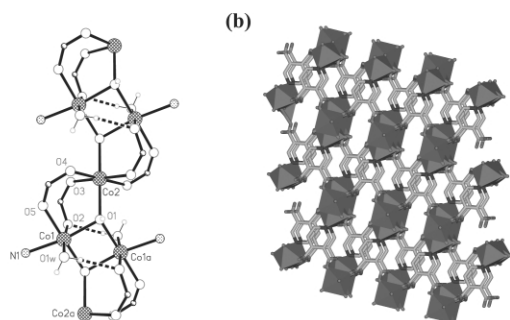
main interactions occur from cobalt polyhedra sharing edges ($d_{Co–Co}$ = 2.988 Å) and vertices ($d_{Co–Co}$ = 3.552 and 3.857 Å). Interestingly, in magnetic hysteresis (Fig. 4b) and *M–H* curve (Figure S6), there are inflection points around 7 kOe. The inflection point would mean an existence of relatively weak antiferromagnetic interaction in this magnetic system. In the first magnetic ordering (0–7 kOe), the interchain interaction is antiferromagnetic. Then the ferrimagnetic chains are coupled antiferromagnetically and the compound shows a weak ferromagnetism based on the magnetic anisotropy of Co(II) ions. Actually, the μ_{eff} *vs. T* plots show a decrease of magnetic momentum below 25 K, which would be due to the antiferromagnetic interchain interaction. When the applied field is over 7 kOe, the interchain antiferromagnetic interaction is overcome by the external magnetic field. Then, a ferrimagnetic phase is formed by ferromagnetic coupling of the ferrimagnetic chains. The compound exhibits a hysteresis loop at 2 K (Fig. 4b) with a large coercive field of 2750 G and the maximum value of magnetization observed of 4.0 B. M. The field-cooled and zero-field-cooled magnetization (FC and ZFC) curves of **1** and **2** measured in a low field of 10 Oe show the absence of spontaneous magnetization in **1**, while the presence of spontaneous magnetization in **2** down to 20.0 K. (shown as inset in Fig. 4) is characteristic of a magnetically ordered state below 20.0 K.

In summary, we have presented hydrothermal transformation of a 2D ferromagnetic coordination polymer into a novel 3D magnetic coordination polymer with 1D ferrimagnet chains by controlled hydrothermal reactions.

Notes and references

‡ Crystal and structure refinement parameters for **1** and **2**. Compound **1**: $C_7H_9CoNO_7$, M = 278.08, triclinic, space group $P\bar{1}$, a = 7.128(1), b = 7.873(2), c = 9.061(2) Å, α = 76.53(3), β = 68.49(3), γ = 76.01(3)°, V = 453.14(17) $Å^3$, Z = 2, D_c = 2.038 g cm^{-3}, R_1 = 0.0381 and wR_2 = 0.0973. Compound **2**: $C_{14}H_{12}Co_3N_2O_{12}$, M = 577.05, triclinic, space group $P\bar{1}$ (No. 2), a = 6.5875(14), b = 6.7860(15), c = 9.975(2) Å, α = 76.123(15), β = 71.782(14), γ = 77.067(16)°, V = 405.80(15) $Å^3$, Z = 1, D_c = 2.361 g cm^{-3}, R_1 = 0.0435, wR_2 = 0.1123. Data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). The structure was solved with direct methods and refined with full-matrix least-squares (SHELX-97). CCDC reference numbers 221040–221041. See http://www.rsc.org/suppdata/cc/b3/b312058a/ for crystallographic data in .cif or other electronic format.

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Fig. 3 The building unit of $Co_3(OH)_2$ chain (a) and 3D coordination network (b) of **2**.
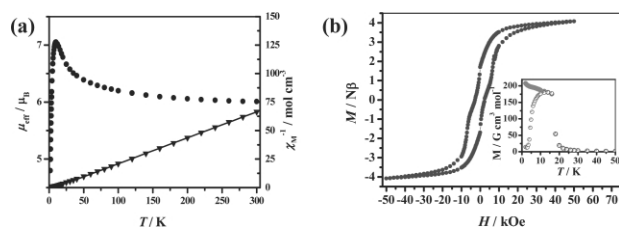

Fig. 4 (a) The temperature-dependent susceptibility of **1**. (b) The magnetic hysteresis at 2.0 K of **2**. Insert: ZFC (□) and FC (●) data collected in an applied field of 10 G.